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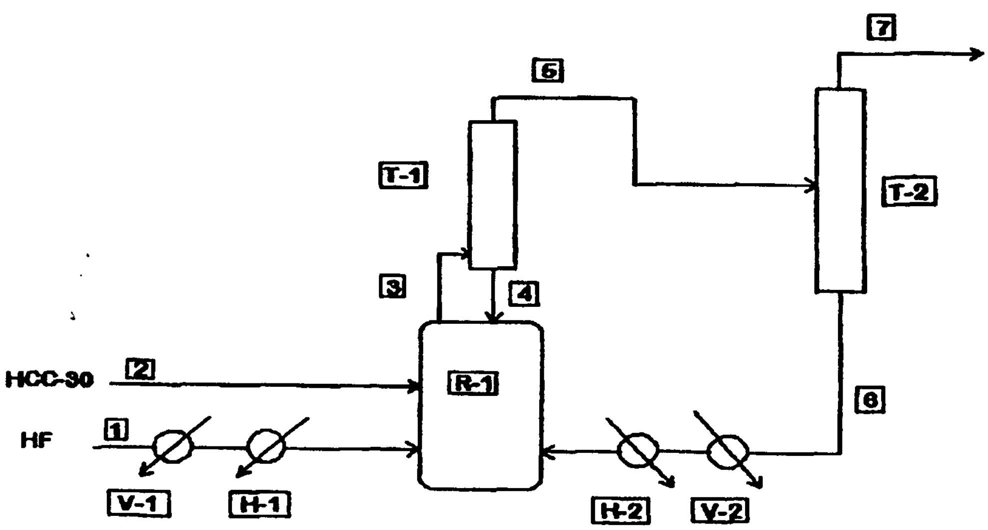
(54) Title: PROCESS FOR THE PREPARATION OF DIFLUOROMETHANE



(57) Abstract

A liquid phase fluorination process for producing difluoromethane without corrosion is provided. In the process of this invention, methylene chloride and hydrogen fluoride are reacted in a reactor made of fluorinated polymer to produce a reaction product while a heated recycle stream of process reactants is fed into the reactor.

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PROCESS FOR THE PREPARATION OF DIFLUOROMETHANE

Field of the Invention

The present invention relates to a hydrofluorination process. In particular, this invention provides a liquid phase hydrofluorination process for producing difluoromethane that exhibits efficient heat transfer and high productivity and that eliminates corrosion in the reactor system.

Background of the Invention

Liquid phase fluorination processes using antimony pentachloride catalysts to produce chlorofluorocarbons ("CFC's") and hydrochlorofluorocarbons ("HCFC's") are well known. CFC's and HCFC's have been implicated in the depletion of the earth's ozone layer and, thus, a need has developed for processes for the production of hydrofluorocarbons ("HFC's"), which are believed not to deplete the ozone layer. One HFC of particular interest is difluoromethane ("HFC-32"). Known liquid phase processes for producing HFC-32 using antimony pentachloride catalysts are very corrosive of the materials of construction used in the process. Therefore, a need exists for a liquid phase fluorination process for producing HFC's that overcomes this problem.

Brief Description of the Drawings

Fig. 1 is a schematic diagram illustrating one embodiment of the process of the invention.

Fig. 2 is a schematic diagram illustrating another embodiment of the process of the invention.

Description of the Invention and the Preferred Embodiments

It has been discovered that a liquid phase fluorination process for producing HFC's without corrosion, but that maintains high productivity and efficient heat transfer may be carried out by heating a recycle of process reactants. The process of this invention comprises, consists essentially of, and consists of reacting methylene chloride ("HCC-30") and hydrogen fluoride in a reactor made of fluorinated polymer to produce a reaction product and feeding concurrently a heated recycle stream of process reactants into the reactor.

For purposes of the invention, by "process reactants" is meant at least one of hydrogen fluoride, HCC-30, monochloromonofluoromethane ("HCFC-31"), and catalyst. Also, for purposes of this invention, by "made of a fluorinated polymer" means that the reactor is constructed of a fluorinated polymer, the reactor is a metal shell lined with a fluorinated polymer, or the reactor is a metal shell lined with a first layer that is a fluorinated polymer and a second layer that is made of carbon bricks or rings, such as graphite, KARBATE®, and the like. Suitable metals for the reactor metal shell may be any of the conventional materials of construction including, without limitation, carbon steel, stainless steel, INCONEL 600®, INCOLOY 825®, MONEL®, and HASTELLOY®.

Suitable fluorinated polymers useful in the reactor will be apparent to those ordinarily skilled in the art. Illustrative polymers include, without limitation, polytetrafluoroethylene polymer, perfluoroalkoxy polymer, ethylene tetrafluoroethylene polymer, vinylidene fluoride polymer, ethylene hexafluoropropylene polymer and the like. Preferably, polytetrafluoroethylene polymer is used.

The liquid phase fluorination reaction preferably takes place in the presence of an effective amount of any suitable fluorination catalyst. Suitable fluorination catalysts include, without limitation, antimony halide catalysts as well as

molybdenum, titanium, tantalum, tin, niobium, and iron catalysts. The invention may find its greatest utility with antimony pentachloride catalyst. The catalyst may be treated prior to use by any known pretreatment method. The amount of catalyst used is an amount effective to catalyze the fluorination of the HCC-30.

Suitable corrosion resistant equipment is used in carrying out the process of the invention. In the process, the HCC-30 and hydrogen fluoride are reacted in a reactor made of fluorinated polymer. The fresh hydrogen fluoride is vaporized and superheated, prior to being fed into the reactor, to a temperature such that the hydrogen fluoride is superheated above its saturation point. Preferably, the fresh hydrogen fluoride is fed into the reactor through an eductor or sparger to promote mixing within the reactor. Reaction temperatures may be from about 70 to about 110° C, preferably from about 75-95° C. The reactor temperature and pressure are maintained such that at least a portion of the hydrogen fluoride in the reactor is maintained in the liquid state.

Reacting the HCC-30 and hydrogen fluoride in the presence of the catalyst produces a reaction product that is a vapor mixture containing the desired product, reaction intermediates, unreacted starting materials and catalyst. The vapor is sent to a distillation column, or other convenient apparatus, for separation. The bottom section and piping connecting the distillation column with the reactor preferably are made of fluorinated polymer. The column bottoms stream, containing the process reactants is recycled back to the reactor. Additionally, a portion of the reactor liquid may be taken from the reactor, vaporized and superheated, and then returned to the reactor at a temperature of less than about 350° F, preferably less than about 250° F.

In all embodiments, the recycle stream of process reactants is heated, meaning that the recycle stream is returned to the reactor at a temperature effective

to maintain a reactor temperature sufficient to produce enough vapor and liquid flow in the first distillation column to effect the separation desired. One ordinarily skilled in the art will be able to readily determine the temperature to which to heat the process reactants by a consideration of the temperature desired to be maintained in the reactor and the amount of vapor needed to be generated so that the first distillation column may effect an efficient separation. Generally, the temperature of the process reactants recycle stream fed into the reactor is between about 100 and about 200 °C, preferably about 130 and about 180 °C.

In one embodiment, fresh hydrogen fluoride, fresh HCC-30, and a recycle stream containing mainly hydrogen fluoride, HCFC-31, and HCC-30, is fed to a reactor made of fluorinated polymer. The fresh hydrogen fluoride and the recycle stream are vaporized and superheated, together or separately, to a temperature required to maintain the reaction mixture in the reactor at the desired reaction temperature. The vaporizer and super heater may be combined into a single heat exchanger. The superheated vapors are introduced into the reactor by any convenient means, preferably through a sparger, such as a perforated pipe or through an eductor to promote mixing and heat transfer into the reactor. The fresh HCC-30 preferably is not heated prior to feeding it into the reactor.

The reactor is connected by a pipe to a first distillation column and, through this pipe, the liquid reflux from the bottom of the column, the column bottoms, is sent back to the reactor through the same pipe or through a second pipe. The distillation column is equipped with a condenser supplied with any convenient means of cooling to produce the reflux. From the top of the column, the column overhead which is the crude product is withdrawn. The column overhead from this column contains hydrogen chloride, HFC-32, HCFC-31, HCC-30, and hydrogen fluoride. This overhead is fed into a second distillation column to separate the HFC-32 and hydrogen chloride in the column overhead to be sent

for further purification. The remaining material, containing hydrogen fluoride, HCFC-31, and HCC-30, is withdrawn from the bottom of the second distillation column and recycled to the reactor after vaporizing and superheating as described.

In another embodiment, the overhead of the first distillation column is fed into a second column to separate the hydrogen chloride as the second column overhead. The remaining material, hydrogen fluoride, HFC-32, HCFC-31, and HCC-30, is withdrawn as the column bottoms and fed into a third distillation column. In the third column, HFC-32 product is separated as the overhead and sent for further purification. The bottoms of the column is recycled to the reactor after vaporizing and superheating.

The invention will be clarified further by the following non-limiting examples.

Examples

Example 1

An apparatus arranged as shown in Fig. 1 is used to produce HFC-32. Referring to Fig. 1, fresh hydrogen fluoride is vaporized in heat exchanger V-1 and superheated in super heater H-1 to about 175° C. The superheated hydrogen fluoride is fed along with liquid HCC-30, stream 2, into reactor R-1, which reactor contains antimony pentachloride catalyst and operates at a temperature of about 90° C and a pressure of between 100 - 300 psig, the pressure maintained so as to keep some of the hydrogen fluoride in the reactor as a liquid.

The vapor generated from the reaction mixture, containing hydrogen chloride, HFC-32, HCFC-31 and HCC-30 and hydrogen fluoride as well as entrained catalyst is sent through a pipe lined with PTFE to the bottom of distillation column T-1, located above reactor R-1 and equipped with an overhead

condenser to produce the liquid reflux. The heat input to the column is provided by the heat contained in the inlet streams to reactor R-1. T-1 is made of fluorinated polymer as are the trays or packing. The liquid from the bottoms of T-1, containing all of the entrained catalyst, and a part of the HCC-30 and hydrogen fluoride, flows back to the reactor by gravity through a pipe made of a fluorinated polymer. The T-1 overhead, containing HFC-32 and hydrogen chloride and part of the HCFC-31 along with HCC-30 and hydrogen fluoride is sent to a second distillation column T-2.

The T-2 heat input is provided by a column reboiler. In T-2, the HFC-32 and hydrogen chloride are separated in the overhead stream and sent for further processing. The T-2 bottoms, containing HCFC-31, HCC-30, and hydrogen fluoride is sent back to reactor R-1 through vaporizer V-2 and superheater H-2. The heat input in both H-2 and V-2 is such that it supplies the heating requirements to maintain the reaction temperature and produces enough vapor and liquid traffic in T-1 to effect the desired separation in T-1. The temperature in the example is about 175° C. The process results in the production of HFC-32 with no corrosion and with increased heat transfer.

Example 2

An apparatus arranged as shown in Fig. 2 is used to produce HFC-32. Referring to Fig. 2, hydrogen fluoride is vaporized in heat exchanger V-1 and superheated in superheater H-1 to about 175° C. The superheated hydrogen fluoride is fed along with HCC-30, and into reactor R-1, which reactor contains antimony pentachloride catalyst and operates at a temperature of about 90° C and a pressure of about 100-300 psig, so as to keep some of the hydrogen fluoride in Reactor R-1 in the liquid state.

Vapor from reactor R-1, containing hydrogen chloride, HFC-32, HCFC-31, HCC-30, hydrogen fluoride and entrained catalyst is sent to T-1, a first distillation column which is configured and outfitted as in Example 1. The bottoms from column T-1, containing HCC-30 and hydrogen fluoride are sent back to reactor R-1 as in Example 1. The T-1 overhead, containing HFC-32, hydrogen chloride, HCFC-31, HCC-30 and hydrogen fluoride is sent to a second column, T-2.

T-2 separates the hydrogen chloride as the column overhead and the bottoms stream, containing HFC-32, HCFC-31, HCC-30 and hydrogen fluoride is fed to a third distillation column T-3. Heat input to columns T-2 and T-3 is supplied by column reboilers. T-3 is operated at a higher pressure than reactor R-1 and separates HFC-32 in the overhead stream. The T-3 bottoms stream, containing HCFC-31, HC-30, and hydrogen fluoride is sent to reactor R-1 through combined vaporizer and superheater H-2 at a temperature sufficient to supply the heating requirements to maintain reaction temperature and produce enough vapor in T-1 to effect the desired separation.

What is claimed is:

1. A process comprising the steps of:

(a.) reacting methylene chloride and hydrogen fluoride in a reactor made of a fluorinated polymer to produce a reaction product; and

(b) feeding concurrently a heated recycle stream of process reactants into the reactor.

2. The process of claim 1 wherein the reacting of methylene chloride and hydrogen fluoride is carried out in the presence of an effective amount of a fluorination catalyst.

3. The process of claim 1 wherein the process reactants recycle stream is heated to a temperature of about 100 to about 200 ° C.

4. The process of claim 1 wherein the process reactants recycle stream is fed into the reactor through a sparger or an eductor.

5. The process of claim 1 wherein step (b) comprises the steps of:

(i) distilling the reaction product in a first distillation column to produce a first column bottoms product that is recycled to the reactor and a first column overhead product comprising hydrogen chloride, difluoromethane, monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(ii) distilling the first column overhead in a second distillation column to separate a mixture comprising difluoromethane and hydrogen chloride as a second column overhead from a second column bottoms product comprising monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(iii) vaporizing and superheating the second column bottoms product; and

(iv) recycling the vaporized and superheated second column bottoms product to the reactor.

6. The process of claim 1 wherein step (b) comprises the steps of:

(i) distilling the reaction product in a first distillation column to produce a first column bottoms product that is recycled to the reactor and a first column overhead product comprising hydrogen chloride, difluoromethane, monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(ii) distilling the first column overhead in a second distillation column to separate hydrogen chloride as a second column overhead from a second column bottoms product comprising difluoromethane, monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(iii) distilling the second column bottoms product in a third distillation column to separate difluoromethane as a third column overhead from a third column bottoms product comprising monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(iv) vaporizing and superheating the third column bottoms product; and

(v) recycling the vaporized and superheated third column bottoms product to the reactor.

7. A process comprising the steps of:

(a.) reacting methylene chloride and hydrogen fluoride in the presence of an effective amount of a fluorination catalyst and in a reactor made of a fluorinated polymer to produce a reaction product; and

(b.) distilling the reaction product in a first distillation column to produce a first column bottoms product that is recycled to the reactor and a first column overhead product comprising hydrogen chloride, difluoromethane, monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(c.) distilling the first column overhead in a second distillation column to separate a mixture comprising difluoromethane and hydrogen chloride as a second column overhead from a second column bottoms product comprising monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(d.) vaporizing and superheating the second column bottoms product; and

(e.) recycling the vaporized and superheated second column bottoms product to the reactor.

8. The process of claim 7 wherein the first and second column bottoms streams are heated before being recycled to the reactor to a temperature of about 100 to about 200° C.

9. A process comprising the steps of:

(a.) reacting methylene chloride and hydrogen fluoride in the presence of an effective amount of a fluorination catalyst and in a reactor made of a fluorinated polymer to produce a reaction product; and

(b.) distilling the reaction product in a first distillation column to produce a first column bottoms product that is recycled to the reactor and a first column overhead product comprising hydrogen chloride, difluoromethane, monochloromonofluoromethane, methylene chloride. and hydrogen fluoride;

(c.) distilling the first column overhead in a second distillation column to separate hydrogen chloride as a second column overhead from a second column bottoms product comprising difluoromethane, monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(d.) distilling the second column bottoms product in a third distillation column to separate difluoromethane as a third column overhead from a third column bottoms product comprising monochloromonofluoromethane, methylene chloride, and hydrogen fluoride;

(e.) vaporizing and superheating the third column bottoms product; and

(f) recycling the vaporized and superheated third column bottoms product to the reactor.

10. The process of claim 9 wherein the first, second, and third column bottoms streams recycled to the reactor are heated to a temperature of about 100 to about 200° C.

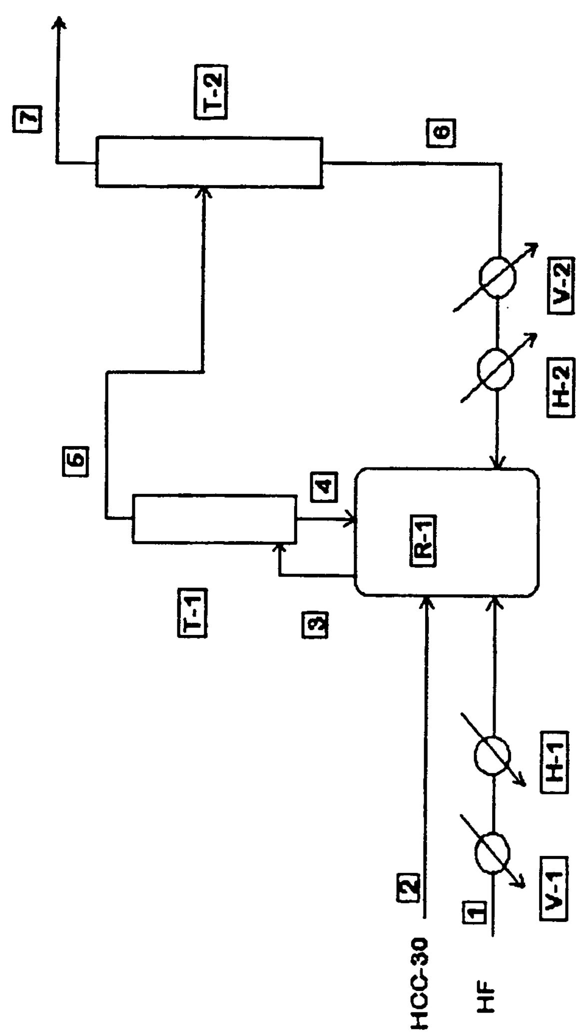
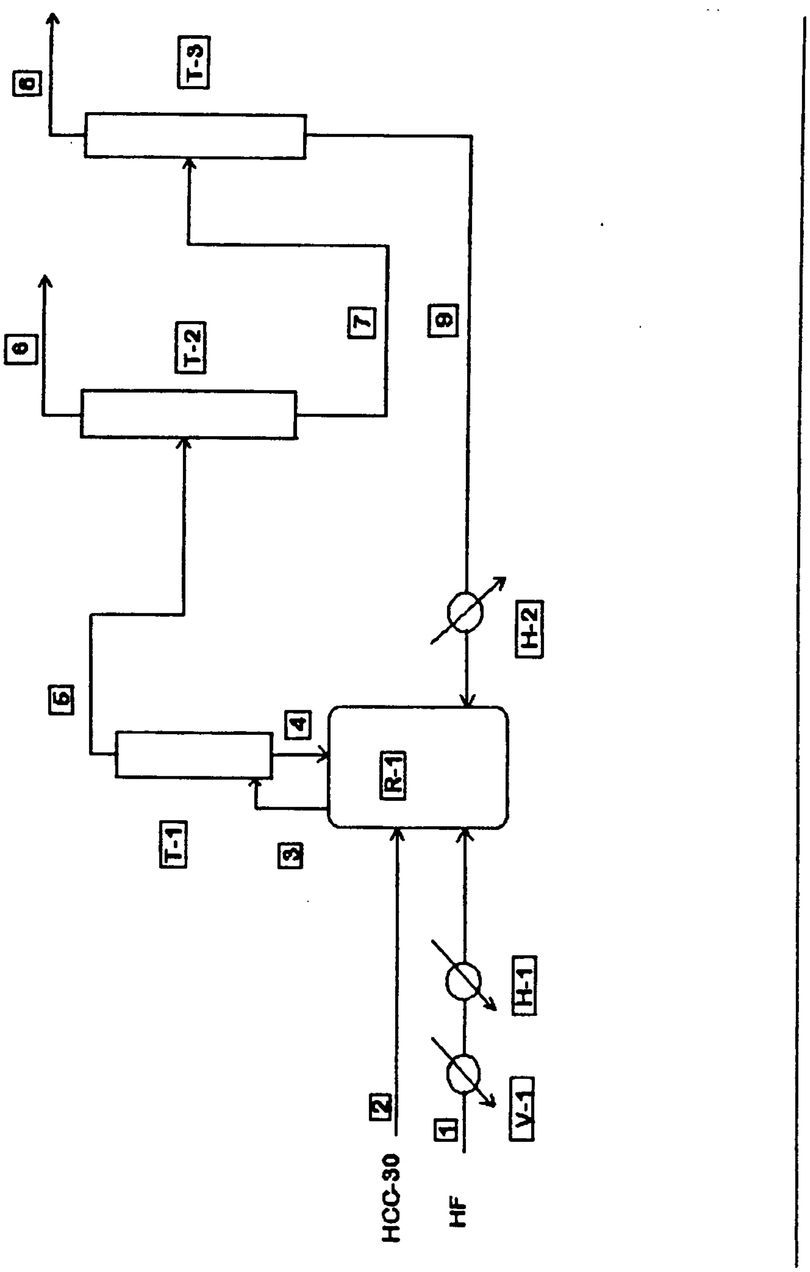


FIGURE 1

FIGURE 2



INTERNATIONAL SEARCH REPORT

Inte onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/20 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 805 136 A (ATOCHEM ELF SA) 5 November 1997 see column 6, line 48 - line 51; claim 1; figure 1	1-10
X	WO 97 11043 A (ALLIED SIGNAL INC) 27 March 1997 see page 3, line 11 - line 13; claim 1	1-10
A	EP 0 767 158 A (DAIKIN IND LTD) 9 April 1997 see page 3, line 35; claim 7	1-10
A	US 5 495 057 A (NAM KYUNG H ET AL) 27 February 1996 see figure 1	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 March 1999	15/03/1999

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Information on patent family members

International Application No
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